Structural features of selenate based {Mo$_{132}$} keplerate capsules

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Supporting information

Table S1. Crystal data and structure refinement

Fig. S1. IR spectra of keplerate compounds **1** and **2**.

Fig. S2. (a) Raman spectra of **2** in aqueous solution (*black*) and in solid state (*red*). (b) Raman spectra of **1** (*blue*) and **2** (*black*) in aqueous solution.

Fig. S3. The contacts between keplerate anions.

Fig. S4. Comparison of experimental and calculated X-ray diffraction patterns for compound **2**.

Fig. S5. Comparison of experimental and calculated X-ray diffraction patterns for compound **3**.

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Fig. S6. Nitrogen adsorption-desorption isotherms at 77 K.

Fig. S7. Carbon-dioxide adsorption-desorption isotherms at 195 K.

Table S2. The parameters of porous structure of samples under investigation.

Table S1. Crystal data and structure refinement for **2-4**

	2	3	4
Chemical formula	$Mo_{132}N_{25.80}O_{628.56}Se_{30}$	$C_{21.80}H_{130.80}Cl_3Mo_{132}N_{65.40}O_{581.40}Se_{30}$	$Mo_{132}N_{32.70}O_{594.24}Se_{30}$
M_r	25451.30	25751.54	24998.85
Crystal system, space group	Trigonal, $R\bar{3}{:}H$	Trigonal, $R\bar{3}c{:}H$	Trigonal, $R\bar{3}{:}H$
Temperature (K)	130	100	130
a, c **(Å)**	32.7739 (5), 73.5789 (11)	50.337 (7), 61.099 (12)	32.6962 (5), 74.0599 (12)
V **(Å³)**	68445 (2)	134072 (46)	68566 (2)
Z	3	6	3
Radiation type	Mo $K\alpha$	Synchrotron, $\lambda = 0.79272$ Å	Mo $K\alpha$
μ **(mm⁻¹)**	3.03	4.16	3.02
Crystal size (mm)	$0.30 \times 0.20 \times 0.20$	$0.30 \times 0.20 \times 0.20$	$0.40 \times 0.20 \times 0.20$
Diffractometer	New Xcalibur, AtlasS2	Rayonix SX-165 CCD	New Xcalibur, AtlasS2
Radiation source	fine-focus sealed tube	synchrotron	fine-focus sealed tube
Absorption correction	Multi-scan *CrysAlis PRO* 1.171.38.41 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	Multi-scan XDS (Kabsch, 2010)	Multi-scan *CrysAlis PRO* 1.171.38.41 (Rigaku Oxford Diffraction, 2015) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.967, 1.000	0.846, 1.000	0.857, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	51926, 27808, 18484	287412, 34107, 23366	49870, 27083, 20284
R_{int}	0.038	0.078	0.020
θ **values (°)**	$\theta_{max} = 25.4$, $\theta_{min} = 3.3$	$\theta_{max} = 31.0$, $\theta_{min} = 1.4$	$\theta_{max} = 25.4$, $\theta_{min} = 3.4$
$(\sin\theta/\lambda)_{max}$ **(Å⁻¹)**	0.602	0.650	0.602
Range of h, k, l	$-24 \le h \le 36$, $-33 \le k \le 39$, $-73 \le l \le 88$	$-65 \le h \le 59$, $-65 \le k \le 65$, $-78 \le l \le 79$	$-15 \le h \le 38$, $-33 \le k \le 33$, $-74 \le l \le 89$
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.070, 0.244, 1.15	0.092, 0.319, 1.21	0.072, 0.234, 1.05
No. of reflections, parameters, restraints	27808, 1288, 24	34107, 1294, 90	27083, 1277, 0
H-atom treatment	–	H-atom parameters constrained	–
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.1345P)^2 + 512.9554P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.2P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1222P)^2 + 3703.9001P]$, where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}, \Delta\rho_{min}$ **(e Å⁻³)**	2.09, -3.35	1.81, -4.05	1.51, -3.03

Computer programs: *CrysAlis PRO* 1.171.38.41 (Rigaku OD, 2015), Marccd (Doyle, 2011), XDS (Kabsch, 2010), *SHELXS2014* (Sheldrick, 2014), *SHELXT2018* (Sheldrick, 2015), *SHELXL2014* (Sheldrick, 2014), *SHELXL2018* (Sheldrick, 2015), ShelXle (Hübschle, 2011), CIFTAB-2014 (Sheldrick, 2014), CIFTAB (Sheldrick, 2015).
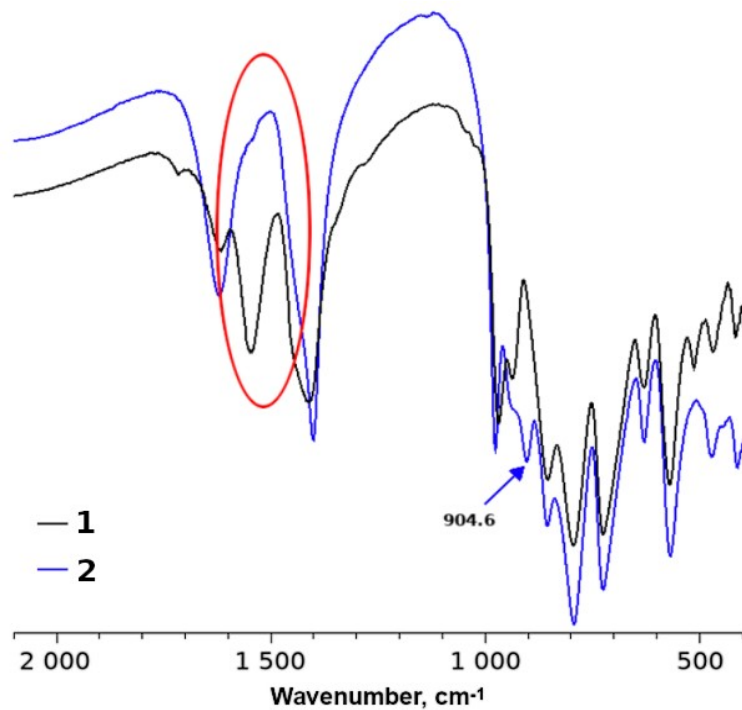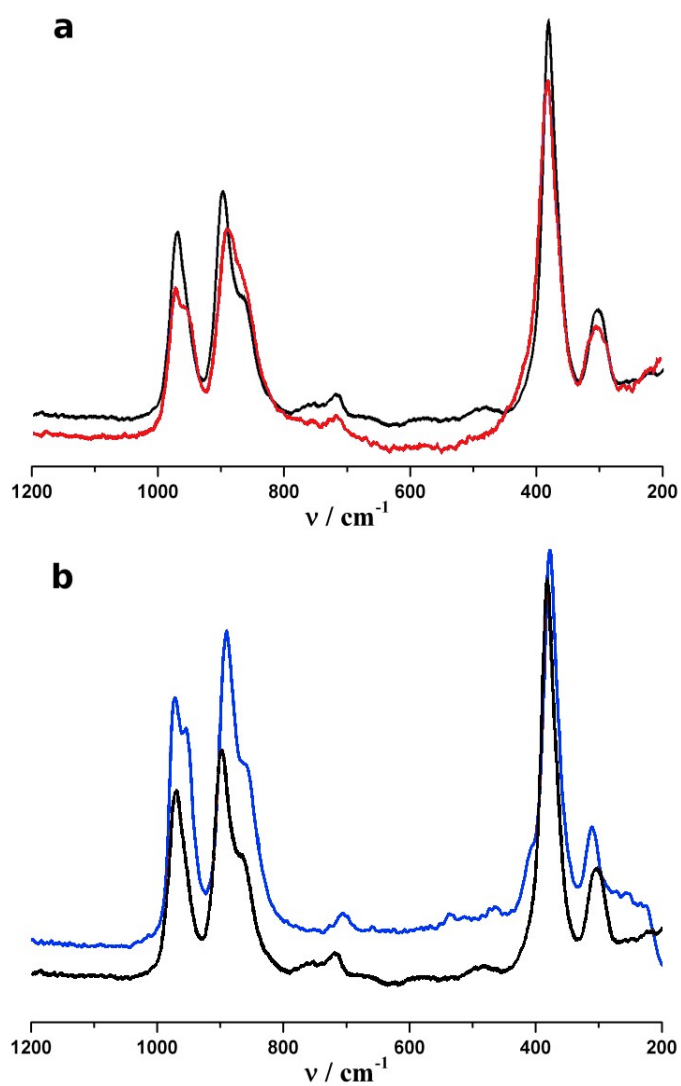
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Fig. S2. (a) Raman spectra of **2** in aqueous solution (*black*) and in solid state (*red*). (b) Raman spectra of **1** (*blue*) and **2** (*black*) in aqueous solution.
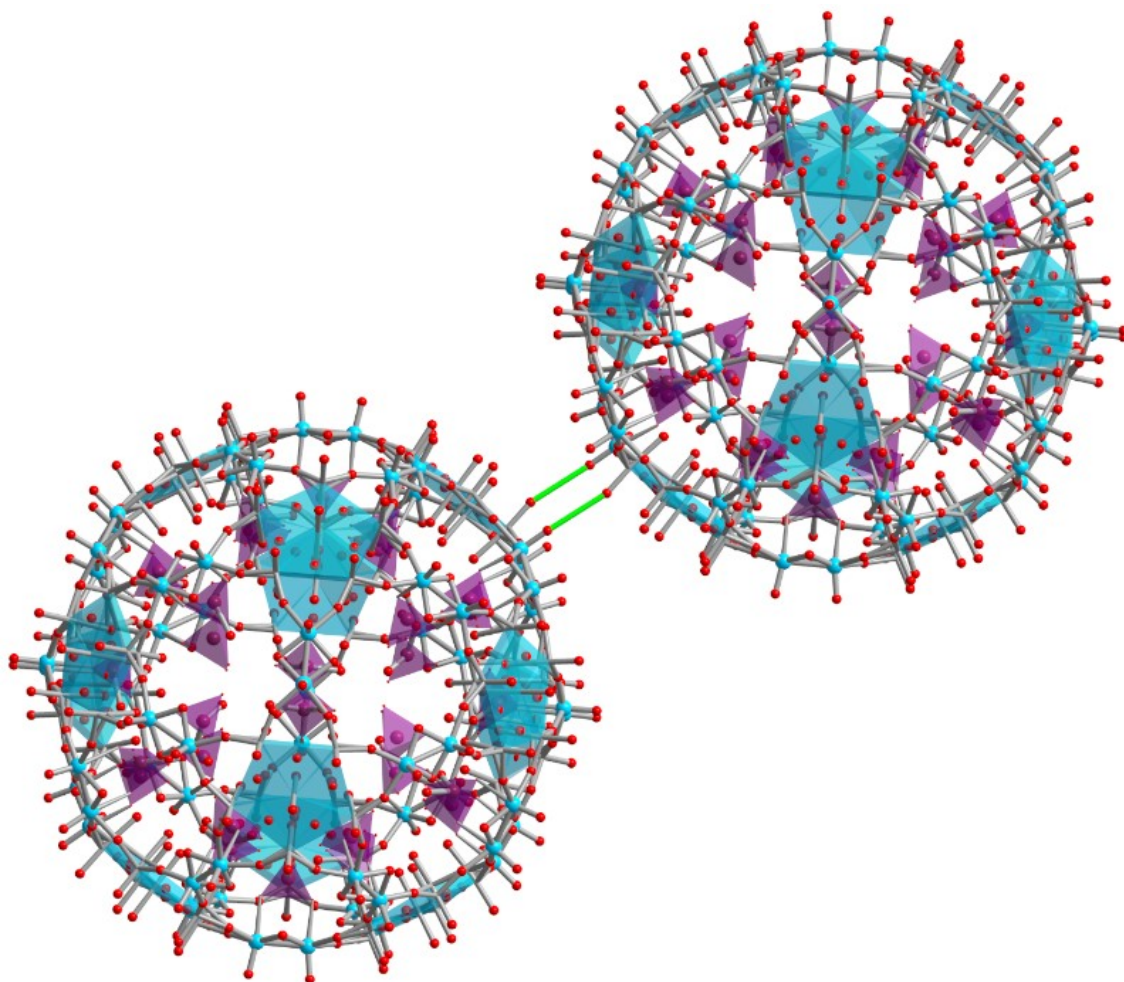
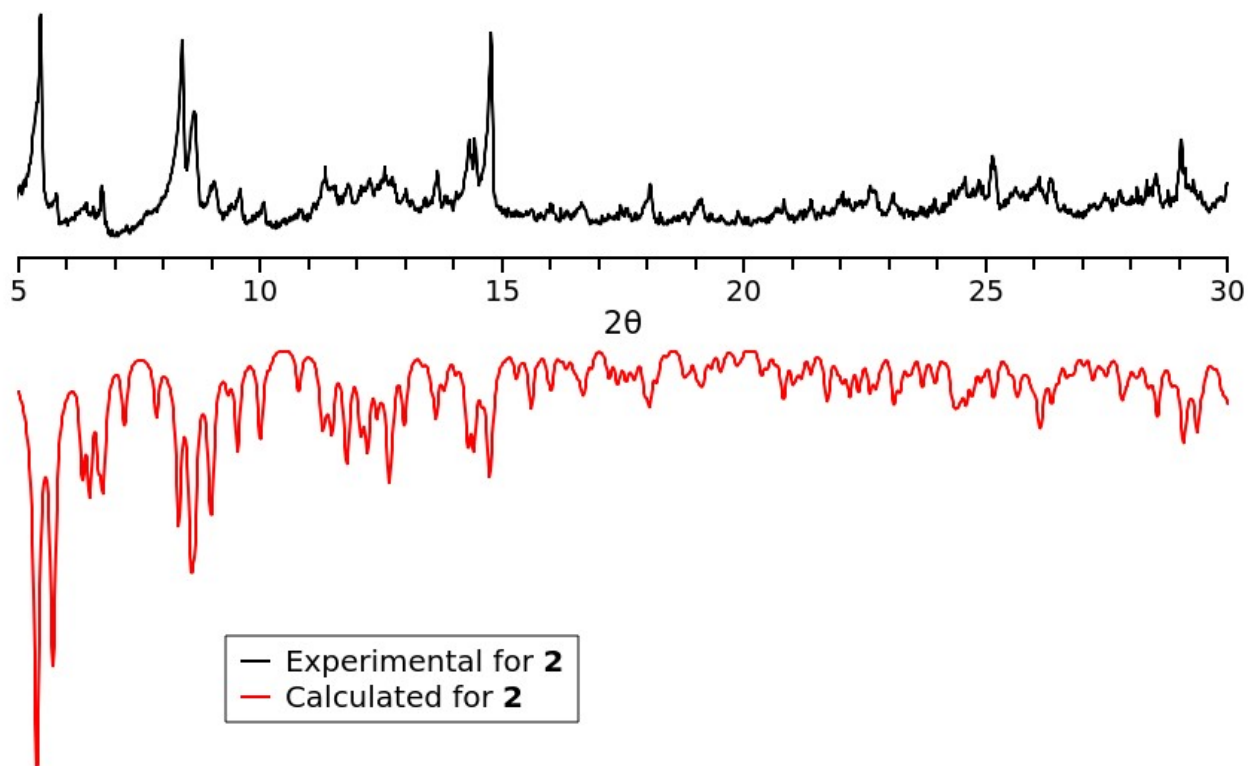**Fig. S3**. The contacts between keplerate anions.

Fig. S4. Comparison of experimental and calculated X-ray diffraction patterns for compound **2**.
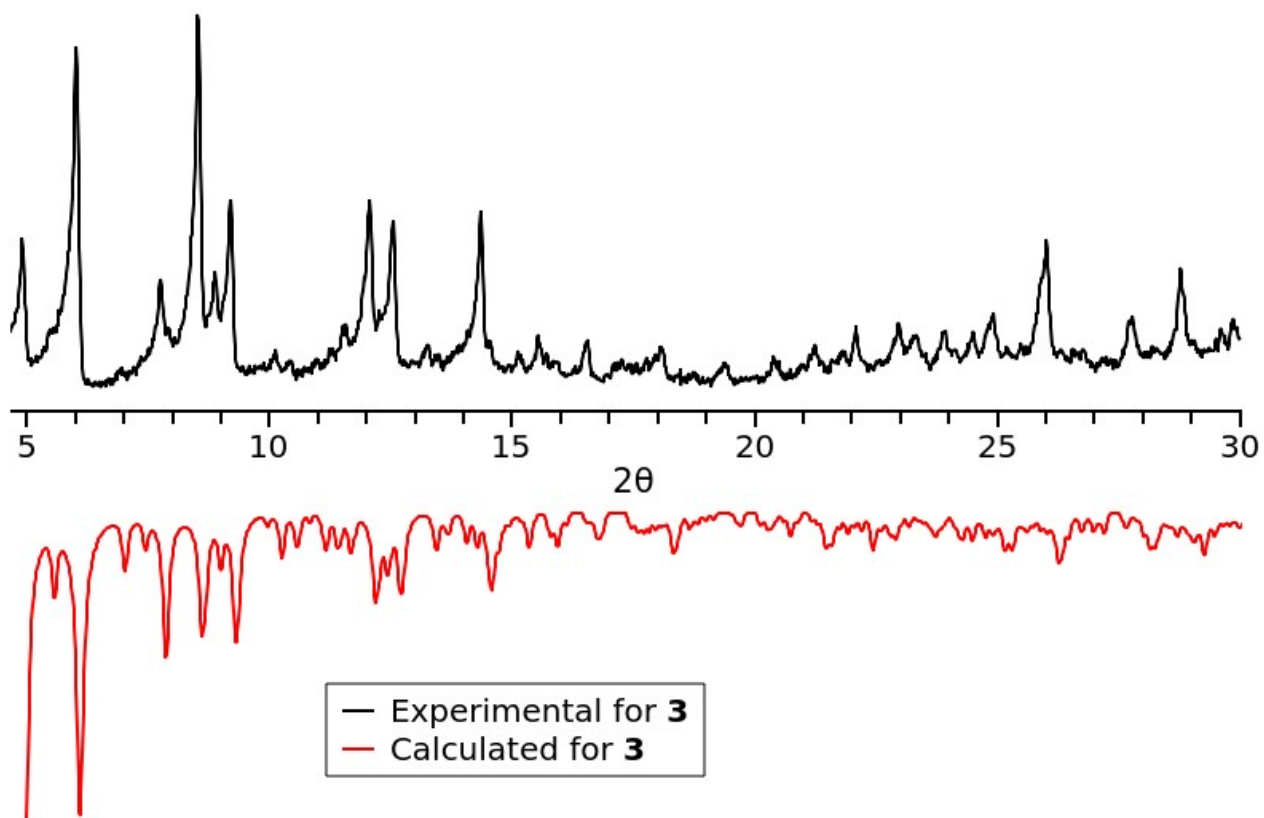
Fig. S5. Comparison of experimental and calculated X-ray diffraction patterns for compound **3**.

Gas adsorption report

Experimental section

Surface Area and Porous Structure. The porous structure was analyzed using the nitrogen adsorption at 77 K and carbon dioxide adsorption at 195 K on a Quantochrome's Autosorb iQ gas sorption analyzer. Initially, compounds were activated under a dynamic vacuum at 130 °C or 150 °C for 6 h. The N_2 and CO_2 adsorption−desorption isotherms were measured within the range of relative pressures from 10^{-6} to 0.995 and from 10^{-3} to 0.995 correspondingly. The specific surface area was calculated from the data obtained using the conventional BET model.

Results

Porous structure (Textural properties)

Measured isotherms of nitrogen adsorption at 77 K and carbon dioxide adsorption at 195 K are represented in Fig. S6, S7. Compounds under investigation are possessing type III isotherms according to official IUPAC classification, which is typical for non-porous compounds with relatively weak adsorbate–adsorbent interactions. Calculated BET surface areas are given in Table S2. Because of the absence of significant adsorption of nitrogen (kinetic diameter 0.364 Å) we tried to study the carbon dioxide adsorption, which molecules have lower kinetic diameter (0.33 Å) and often use for textural characterization of ultramicroporous adsorbents. Unfortunately, the carbon dioxide uptake at 195 K on both compounds was also negligible.
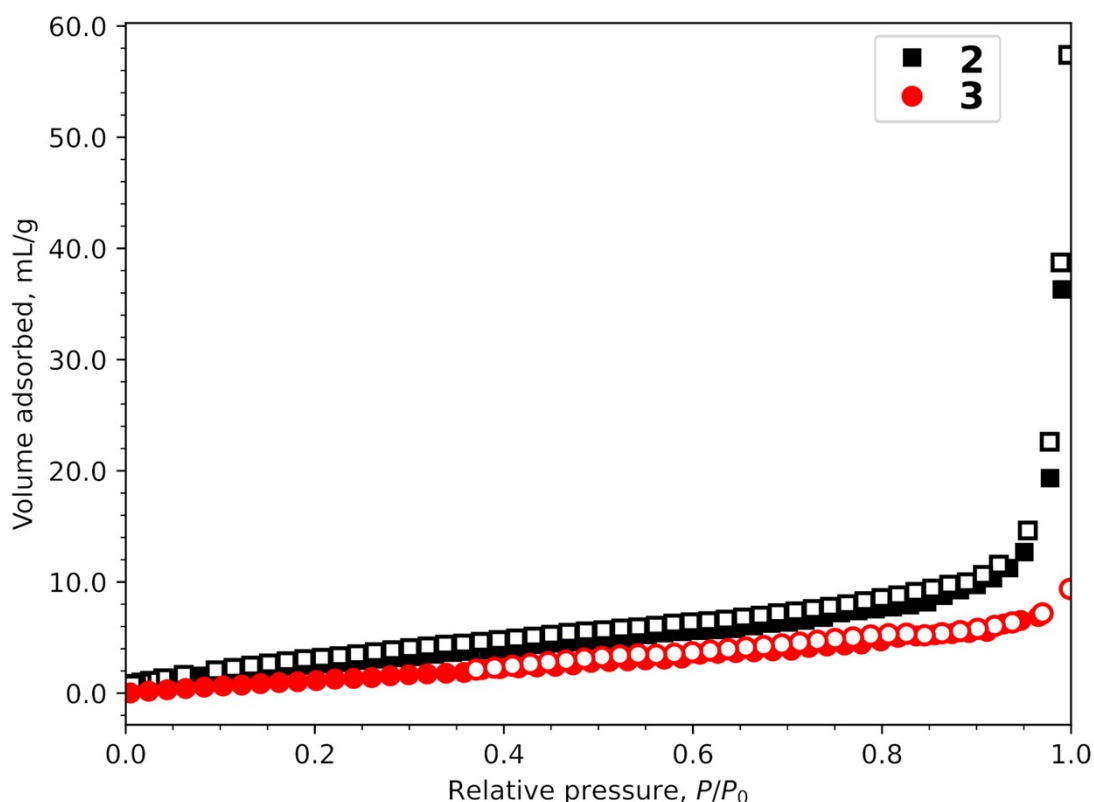

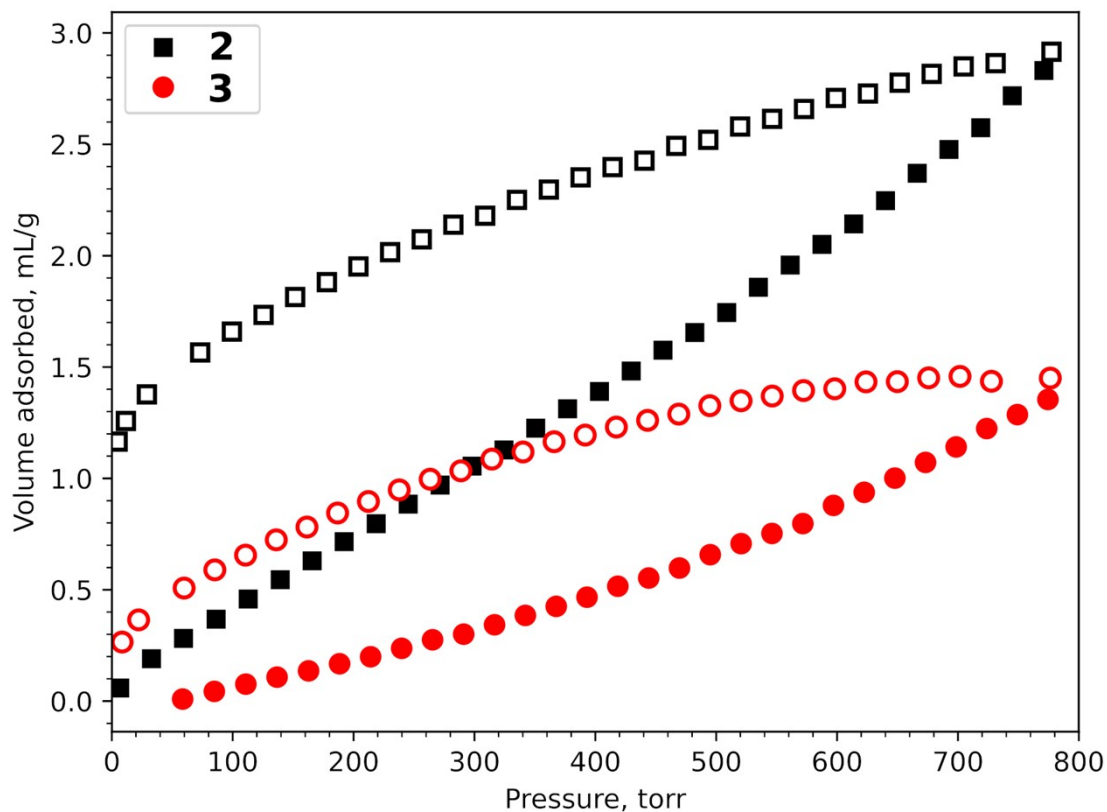**Fig. S6.** Nitrogen adsorption-desorption isotherms at 77 K.

Fig. S7. Carbon-dioxide adsorption-desorption isotherms at 195 K.

Table S2. The parameters of porous structure of samples under investigation.

Sample, gas@temperature	Specific surface area / $m^2 \cdot g^{-1}$	V_{pore} / $cm^3 \cdot g^{-1}$	$V_{ads}(N_2)^a$/ $cm^3(STP) \cdot g^{-1}$
2, N_2@77 K	12.01	≈0.015	9.7
2, CO_2@195 K	3.8	≈0.004	2.6
3, N_2@77 K	8.4	≈0.008	5.5
3, CO_2@195 K	1.8	≈0.002	1.2

[a] total pore volume, measured at $P/P_0 = 0.90$.

So, both compounds are non-porous. Calculated BET surface area is attributed to external surface of crystallites and pore volume is corresponded to inter-crystallite volume due to their dense-packing.